

Separation of Carboxylic Acids from Waste Water via Reactive Extraction

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ABSTRACT

The separation (or removal) of organic residues from aqueous waste streams released from industries is important and essential from the points of view of pollution control and recovery of useful materials. The disposal of waste waters containing most widely-used industrial organic acids such as acetic acid, formic acid and propionic acid has been recognized as a significant expense to the industry and environment. This paper presents a state-of-the-art review on the development of techniques for the separation of carboxylic acids from waste water. Available conventional techniques including fractional distillation, liquid extraction, adsorption, precipitation, ion exchange, etc. have been discussed emphasizing the major drawbacks of these methods. A new method – reactive extraction - for extracting carboxylic acids from dilute aqueous solutions using a chemical extractant is described and compared with the other conventional techniques. Reactive extraction is an efficient, economical, and environmental friendly method for separation of acids from waste water streams.

Keywords: Waste Water; Carboxylic acids; Separation Processes; Reactive Extraction; Extractant.

1. Introduction

Aqueous waste discharged from chemical plants typically contains low levels (a few percent or less) of small organic compounds such as carboxylic acids amines, alcohols and aldehydes. Whenever detailed characterization of industrial waste water streams has been carried out, one of the organic acids commonly found in significant concentrations is acetic acid. The concentration of these acids can differ significantly. Monocarboxylic acids such as formic acid, acetic acid or propionic acid are fundamental materials in the chemical industry. The organic acids are most widely used in the field of food and beverages as an acidulant and also in pharmaceutical and chemical industries. Carboxylic acids are classified by the chemical structure R-COOH. In this acid form, they are fully hydrocarbon soluble. Only those organic acids with a carbon count of five or less exhibit water solubility. However, an important characteristic of organic acids is that alkali metal salts of these compounds are readily soluble in water and insoluble in hydrocarbon media. Formic acid is used in the textile industry, in

tanning, in rubber processing and in the manufacture of pharmaceuticals. Acetic acid is used in the synthesis of acetyl cellulose and plastics and also in the food industry, as well as in the printing and dyeing industries. Calcium and potassium salts of propionic acid are used in the food industry as preservatives (Cai *et. al.* 2001, Jaung and Wu, 1999). Processing in petrochemical plants, and wood pulping mills often generate aqueous effluent streams containing carboxylic acids, particularly acetic acid (Technical Bulletin, 1999). An aspect of high environmental importance is the recycling of acids from effluents rather than their neutralisation to form sludges for disposal.

2. The need for recovery of carboxylic acids

Advanced treatment of waste water streams containing significant amount of acetic acid and formic acid to meet future water quality standards has been recognized as a significant expense to the industry and environment. The cost of treatment of waste streams containing acetic acid using a conventional activated sludge biological treatment system is between 4 to 10 cents/kg depending on the concentration and sludge disposal system.

In addition to treatment requirements, the discharge of acetic acid containing waste water represents the loss of valuable resource. Today acetic acid is one of the most important industrial organic acids and consumed worldwide, about half of it in USA. The global demand of acetic acid is around 6.5 million tonnes per year (Mt/a), of which approximately 1.5 Mt/a is met by recycling; the remainder is manufactured from petrochemical feedstocks or from biological sources (Acetic Acid, 2008).

The largest single use of acetic acid is in the production of vinyl acetate monomer that is used for vinyl plastics, adhesives, textile finishes and latex paints and it is closely followed by acetic anhydride and ester production. This acetic anhydride is used for cellulose acetate and pharmaceuticals and plasticizers production. In households diluted acetic acid is often used in descaling agents. In the food industry acetic acid is used under the food additive code E260 as an acidity regulator. The principal use of formic acid is as a preservative and antibacterial agent in livestock feed. it is also widely used to preserve winter feed for cattle. In the poultry industry, it is sometimes added to feed to kill salmonella bacteria (Formic Acid, 2008). Most propionic acid produced is used as a preservative for both animal feed and food for human consumption. For animal feed, it is used either directly or as its ammonium salt. In human foods, especially bread and other baked goods, it is used as its sodium or calcium salt. Propionic acid is also useful as a chemical intermediate. It can be used to modify synthetic cellulose fibers. It is also used to make pesticides and pharmaceuticals. The esters of propionic acid are sometimes used as solvents or artificial flavorings (Kumar and Babu, 2008a).

3. Techniques for separation of carboxylic acid from waste water

As a result of a thorough waste characterization program and preliminary evaluation of the costs that would be associated with secondary treatment, the work toward developing removal and recovery of waste stream components is started in 1974. the separation of monocarboxylic acids from waste water has been important and essential from the points of view of pollution control and industrially for more than a century (Helsel, 1977). Several physical separation techniques such as liquid extraction, ultra filtration, reverse osmosis,

electro-dialysis, direct distillation, liquid surfactant membrane extraction, anion exchange, precipitation and adsorption have been employed to remove carboxylic acids from aqueous solution.

3.1 Membrane processes

A potentially effective treatment of these waste solutions is to use membranes to remove and recover the organic contaminants (Sirman *et al* 1991). Established membrane processes that have been utilized for waste water treatment include ultra filtration, reverse osmosis (Timmer *et al* 1994), electro-dialysis (Lee *et al* 1998), nanofiltration (Timmer *et al* 1994) and pervaporation. The small size of the organics excludes the use of ultrafiltration and microfiltration, and the osmotic pressure limitation from high salt content makes reverse osmosis impractical. Supported polymeric liquid membrane can be effective for treating the types of waste stream described above (Ho, 1999). Attractive features of this membrane process include the ability to recover the acids in concentrated form for reuse or more economical disposal of waste, low pressure (ambient) operation, simple scale-up using commercial hollow fiber modules, and ease of in-situ regeneration of the polymeric liquid. The process has shown treatment feasibility for several types of aqueous waste streams, but it is not cost effective. In these processes, the problem of membrane fouling which requires frequent cleaning of the dialyzer. It gives a higher extent of acids separation but with increased power and energy consumption. The drawbacks are being of hindered implementation, mainly complexity of operation and swelling in liquid surfactant membrane. However, supported liquid membrane often suffers from membrane instability.

3.2 Distillation

Water is the lower boiling component and relative volatility of water to acetic acid is very low. Although acetic acid and water do not form an azeotrope, it is necessary to have a large number of equilibrium stages and a very high reflux ratio to obtain glacial grade acid by simple distillation. As an alternative to fractionation, to reduce energy consumption, azeotropic dehydration can be employed with addition of another liquid. In this technique, the entrainer carries the water overhead in the distillation column with the mixture being phase separated after condensation and entrainer being returned to the column. It is effective only for high concentration of acids (Helsel, 1977, Cockrem and Johnson, 1991).

3.3 Liquid-liquid extraction

For intermediate concentrations between 5 to 50%, liquid-liquid extraction is usually employed, typically followed by azeotropic distillation. Pure solvents such as low molecular weight esters, ethers, alcohols, ketones and hydrocarbons etc. are unable to give sufficient distribution coefficients for carboxylic acids. The solvent extract stream, containing the acid removed from waste stream and some dissolved water is sent to a distillation column where solvent and water is taken overhead (Wardell and King, 1978 and Baniel 1982).

3.4 Adsorption

Carboxylic acids may be recovered by adsorption on solid adsorbent. Kawabata et al. (1982) separated carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts. The selected elutants

were aliphatic alcohol, aliphatic ketones and carboxylic esters. But the cost associated with regeneration of commercial adsorbents make adsorption operation very expensive.

3.5 Precipitation

Pekham describes a process for the purification of lactic acid by precipitation. In the calcium precipitation process, the separation and final purification stages account for up to 50% of the production costs and produces a large quantity of solid waste. So, Conventional calcium precipitation method is simple and reliable but it is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste (Wasewar *et al* 2004).

4. Reactive extraction

Among various available alternate processes for removal of the bioproduct such as carboxylic acids from waste water stream, extraction is often the most suitable one (Kumar and Babu, 2008b) as shown in Fig. 1. Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxyl-carboxylic acids. Reactive Extraction is developed to intensify separation by solvent extraction and represents a connection between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilization of the system components). So a reactive extraction method has been proposed to be an effective primary separation step for the recovery of carboxylic acid from aqueous solution (Cascaval and Galaction 2004).

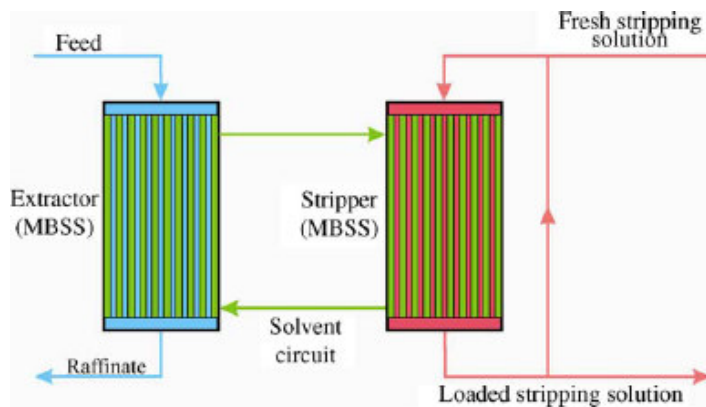


Figure 1. Membrane based Solvent extraction system for separation of carboxylic acids

Advantages of this system include the need for relatively small volumes of solvent; low water miscibility in the system; high degree of phase separation in the system, which allows for smaller extraction equipment; and stability and high boiling point of solvent. After the extraction of organic acids, solvents are regenerated by stripping the acids for recycle in the extraction process. So, cost of separation of these useful products is reduced by using recycled solvents. For that reason the recovery of carboxylic acids, in particular acetic acid and propionic acid is economically advantageous. For example, total recovery costs for a 2% acetic acid stream of $0.0126 \text{ m}^3/\text{s}$ from which 90% of the acetic acid is recovered are given as 12.73 cent/kg. The recovery of other low molecular weight acids is suggested to make this method more economically attractive (Helsel, 1977).

Reactive extraction strongly depends on various parameters such as the distribution coefficient, degree of extraction, loading ratio, complexation equilibrium constant, types of complexes (1:1, 2:1, etc.), rate constant of carboxylic acid-extractant reaction, properties of the solvent (extractant and diluent), type of solvent, temperature, pH and acid concentration (Kahya *et al*, 2001).

The extraction of carboxylic acids is categorized into three groups: (i) acid extraction by solvation with carbon-bonded oxygen-bearing extractants (also inert aliphatic and aromatic hydrocarbons and some of their substituted homologs); (ii) acid extraction by solvation with phosphorus-bonded oxygen-bearing extractants and (iii) acid extraction by proton transfer or by ion pair formation, the extractant being high-molecular weight aliphatic amines (Kertes and King 1986). The distribution coefficients of carboxylic acids between the aqueous phases and organic phases with only first categorized solvents are very low as shown in table 2 (Schugeri, 1994).

Table 2. Distribution coefficients (K_D) of carboxylic acids between the water and organic solvents at 25 °C

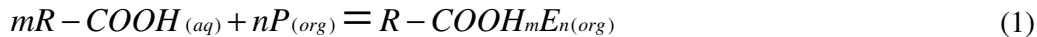
Carboxylic Acid	Solvent	K_D
Acetic acid	Ethers (C4-C8)	0.14
Propionic acid	n-Hexane	0.005
	Cyclohexane	0.006
	Benzene	0.043
	Toluene	0.034
	Xylene	0.03
	Carbon tetrachloride	0.015
	Chloroform	0.11
	Nitrobenzene	0.16
	Diethyl ether	1.75
	Diisopropyl ether	0.80
	Methylisobutyl ketone	2.15
	Cyclohexanone	3.30
	n-Butanol	3.20
	n-Pentanol	2.95

Organophosphoric derivatives such as tri-n-octyl phosphine oxide (TOPO), tri-n-butyl phosphate (TBP) and long-chain, aliphatic amines such as lauryl-trialkylmethylamine (Amberlite LA-2), tri-n-octylamine, tri-iso-octylamine, tri-n-(octyl-decyl)-amine (Alamine 336) and quaternary alkylammonium salt (Aliquat 336) are effective extractants for separation of carboxylic acids from dilute aqueous solution (Kertes and King 1986). Generally, extractants are dissolved in a diluent, an organic solvent that dilutes the extractant. It controls the viscosity and density of the solvent phase. However, the chemical structure of a diluent may have various effects connected with the formation of acid-amine complexes in the organic phase. The equilibrium behavior has been studied effectively by postulating the formation of various stoichiometric complexes of acid and extractant (Tamada *et al*, 1991).

4.1 Phosphorus bonded oxygen bearing extractants

Generally speaking, weak organic acids are extracted by organophosphorus compounds with a significantly higher distribution ratio than by carbon-bonded oxygen donor extractants under comparable experimental conditions. The basic donor properties of the phosphorus-bonded oxygen extractants makes the solvation process to be specific, and the number of solvating molecules per extracted acid is experimentally accessible (Kertes and King 1986).

The reactive extraction mechanism with organophosphorus based extractant can be expressed by following interface equilibrium as given in eq. (1):



So, Phosphorus based solvating extractants has opened new avenues in process development and reduced energy and reagent consumption and several studies using these extractants have been made. extraction equilibria of a number of organic acids, like acetic acid, glycolic acid, lactic acid, pyruvic acid, butyric acid, succinic acid, fumaric acid, maleic acid, itaconic acid, tartaric acid, citric acid and isocitric acid with tri-*n*-octylphosphine oxide in hexane has been investigated by Hano *et al.* (1990). Al-Mudhaf *et al.*, (2002) and Cai *et al.*, (2001) using phosphate based extractants showed that tri-*n*-octylphosphine oxide (TOPO) had a higher distribution coefficient than tri-*n*-butyl phosphate (TBP). Wang *et al.*, (2001) has used Cyanex® 923 in kerosene to extract monocarboxylic acids and found that the distribution ratios increased with an increase in the trialkylphosphine oxide concentration but decreased with the carboxylic acid concentration in the aqueous phase. The study has been made to examine the use of the organophosphine oxides, (Cyanex@921 and Cyanex@923) for the extraction of formic, acetic and propionic acids from aqueous solutions (waste water stream) by Wisniewski and Piezchalska (2005).

4.2 Aliphatic amine based extractants

Amines (tri and tertiary) are found to be effective extractants for carboxylic acids. The amines have been favored because of lower cost and generally higher distribution coefficient. Among different amines, extraction with primary amines is characterized by a large mutual solubility of the aqueous and organic phase; secondary amines have the highest reported distribution coefficient, but tend to form amides in the downstream regeneration by distillation; quaternary amines extract acid at both acidic and basic pH via an anion exchange mechanism, but are difficult to regenerate by back extraction with caustic. Consequently, tertiary amines are the most attractive for extraction from aqueous stream on the basis of their low aqueous solubility and intermediate basicity, providing reasonable extracting power along with the possibility of stripping. The extractant must be diluted with an organic solvent to provide suitable physical properties for use in an extraction process (Kertes and King 1986).

The reactive extraction mechanism with amine based extractant can be expressed by following interface equilibrium as given in eq. (2):



Hong and Hong (1999) carried out the Reactive extraction of lactic acid with mixed tertiary amine extractants. The mixture of tripropylamine (TPA) and trioctylamine (TOA) dissolved in 1-octanol/n-heptane was used in the reactive extraction of (L+) lactic acid in aqueous solution. Malmay *et al.* (2001) proposed experimental and mathematical studies for recovery of carboxylic acids from aqueous solutions by liquid-liquid Extraction with a triisooctylamine diluent system. Tamada *et al.* (1991) studied the extraction of acetic acid, lactic acid, succinic acid, malonic acid, fumaric acid, and maleic acid by Alamine 336, an aliphatic, tertiary amine extractant, dissolved in various diluents. Matsumoto *et al.* (2001) studied the extraction of organic acids using both amine based extractant – (tri-n-octylamine) and phosphorus based extractant – (tri-n-butyl phosphate). The design of an amine extraction process requires equilibrium data for the acid-amine (solvent) system used. Equilibria for propionic acid extraction by trioctyl amine in various solvents hexanol, butyl acetate, and petroleum ether have been determined by Wasewar and Pangarkar (2005). Kumar *et al.* (2006) has intensified the recovery of propionic acid using reactive extraction. The conventional solvents, such as simple hydrocarbon, ketone, kerosene oil and alcohol with or/and without Aliquat 336 are used to recover the acids from aqueous solution using reactive extraction.

5. Conclusion

It is important to have an efficient and sustainable technology for the separation of carboxylic acids from the waste water stream from the points of view of pollution control and recovery of useful materials. Monocarboxylic acids such as formic acid, acetic acid or propionic acid are fundamental materials in the effluent of chemical industries. Several physical separation techniques such as liquid extraction, ultra filtration, reverse osmosis, electro-dialysis, direct distillation, liquid surfactant membrane extraction, anion exchange, precipitation and adsorption have been employed to remove carboxylic acids from aqueous solution. Some of these techniques are not environment friendly and others are not cost effective. Reactive extraction with a specified extractant has been proposed as a promising technique for separation of carboxylic acids from waste water. Organophosphoric derivatives and long-chain, aliphatic amines have also opened up new avenues in recovery of carboxylic acids from waste stream with reduced energy and reagent consumption via reactive extraction.

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